Characterization and Development of Measurement Methods for Ambient Nitrogen Dioxide (NO$_2$)

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Research Questions and Motivation:

• How do direct, optical measurements of NO\textsubscript{2} compare with the Federal Reference Method and photolytic conversion techniques?

• What is the optimum method for calibration and span/zero checks for each type of monitor (Gas Phase Titration of NO vs bottled NO\textsubscript{2})?

• EPA’s ORD interest in accurate NO\textsubscript{2} measurements supports:
  • Reference and equivalent method determinations and evaluations
  • EPA’s monitoring networks
  • Ground-based satellite validation work with NASA
Outline

I. NO$_2$ sources, trends, and regulations
II. Gas-phase chemiluminescence measurement methods:
   a. Federal Reference Method
   b. Photolytic conversion
III. Direct, optical techniques:
   a. Cavity ringdown spectroscopy (CRDS)
   b. Cavity attenuated phase shift (CAPS)
IV. Results from DISCOVER-AQ Campaign
V. Preliminary Results from RTP, NC
Atmospheric nitrogen families

\[ \text{NO}_x = \text{NO} + \text{NO}_2 \]  

“nitrogen oxides”

\[ \text{NO}_y = \text{NO}_x + \text{HNO}_3 + \ldots \]  

“total reactive nitrogen”

\[ \text{HONO} + \text{RONO}_2 + \text{RO}_2\text{NO}_2 + \text{NO}_3 + \text{N}_2\text{O}_5 + \text{NO}_3^- (p) \]

\[ \text{NO}_z = \text{NO}_y - \text{NO}_x \]  

“reacted oxides of nitrogen”

• \text{NO}_2 serves as the indicator species for the family of the oxides of nitrogen.
Current NO$_2$ Regulations

• Clean Air Act requires EPA to set National Ambient Air Quality Standards (NAAQS) for criteria pollutants:

<table>
<thead>
<tr>
<th>NO$_2$ Primary Standards</th>
<th>level</th>
<th>averaging time</th>
<th>year implemented</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>53 ppb</td>
<td>Annual</td>
<td>1971</td>
</tr>
<tr>
<td></td>
<td>100 ppb*</td>
<td>1 hr</td>
<td>2010</td>
</tr>
</tbody>
</table>

* The new monitoring locations for the Jan 2010 primary standard will be sited in near roadway locations to capture areas of maximum concentration. (http://epa.gov/ttn/amtic/nearroad.html)

* Continuous monitors capable of hourly data are now necessary.
What are the sources of NO\textsubscript{x}?

Global (natural and anthropogenic):
- Fossil Fuels: 66%
- Soils: 11%
- Lightning: 10%
- Biomass Burning: 14%

anthropogenic (US):
- Utilities (22%)
- Mobile Sources (58%)
- Industrial/commercial/residential combustion (12%)
- Other (8%)

- Primarily emitted as NO
- Emissions reductions aimed at mobile and point sources

Based on IPCC (2001) data
Based on 2002 National Emissions Inventory Data
Emissions of NO$_2$ are declining

- 48% decrease in the national average.
- Achieved by reducing NO$_x$ for O$_3$ purposes (mobile and point source regulations).

Data from EPA’s Air Quality System (AQS)
How is NO\textsubscript{2} (currently) measured?

  - **Gas-phase chemiluminescence**
  - Indirectly measure NO\textsubscript{2} by conversion to NO, then NO is detected by chemiluminescence (NO + O\textsubscript{3} \rightarrow NO\textsubscript{2}\textsuperscript{*}, NO\textsubscript{2}\textsuperscript{*} = excited state);

- **Advantage** \(\rightarrow\) in use since the 1970s (long term record)
- **Disadvantages** \(\rightarrow\) non-specific; indirect
Method has possible interferences

- Non-specific to NO₂ → heated metal catalysts known to convert other NO\textsubscript{y} species to NO.

- Considered an upper limit measurement of NO₂.

Dunlea et al. ACP (2007)
• NO spikes → The indirect determination requires a slowly changing NO\textsubscript{x} distribution. Otherwise, negative spikes of NO\textsubscript{2} are possible:
• Replace the metal bed reducer with a photolysis cell to photolyze NO\(_2\) to NO (NO\(_2\) + \(h\nu\) \(\rightarrow\) NO + O).
  - Use high-power light sources to maximize conversion to NO.

- Advantage \(\rightarrow\) more specific to NO\(_2\)
- Disadvantages \(\rightarrow\) non-unity conversion efficiency; still indirect
UV/Vis Spectroscopy of NO$_2$

Data from Sander et al. (2006)
Cavity ringdown spectroscopy
- instrument manufactured by Los Gatos Research, Inc.

- 10 s time resolution
- Advantage → DIRECT measurement
- Disadvantages → not-necessarily specific to NO₂, but to any molecule that absorbs light at 405 nm
Direct Optical Techniques

• Cavity ringdown spectroscopy
  - instrument manufactured by Los Gatos Research, Inc.

- 10 s time resolution
- Advantage → DIRECT measurement
- Disadvantages → not-necessarily specific to NO₂, but to any molecule that absorbs light at 405 nm
• Cavity attenuated phase shift spectroscopy (CAPS)
  - instrument manufactured by Aerodyne Research, Inc.

  - Advantage → DIRECT measurement
  - Disadvantage → not-necessarily specific to NO₂, but to any molecule that absorbs light at ~450 nm
  - 2 versions: fast response (1 s) and ambient (10 s)
• Cavity attenuated phase shift spectroscopy (CAPS)
  - instrument manufactured by Aerodyne Research, Inc.
  - Advantage → DIRECT measurement
  - Disadvantage → not-necessarily specific to NO$_2$, but to any molecule that absorbs light at ~450 nm
  - 2 versions: fast response (1 s) and ambient (10 s)
NASA DISCOVER-AQ and EPA collaboration

• Supplement the existing local monitoring sites with NO$_2$ measurement technologies → satellite validation.
• First deployment was July 2011 in/around the greater Baltimore/DC metro area.
• Deployed two NO$_x$ monitors: one FRM and one photolytic-chemiluminescence
Results from Padonia, MD Ground Site

[Graph showing NO2 levels with FRM and photo-chemiluminescence data from July 1 to Aug 2, 2011]
Preliminary Results from Padonia, MD Ground Site

\[ \Delta NO_2 = NO_2_{\text{FRM}} - NO_2_{\text{photo}} \]

- The interference in the FRM monitor over predicts by \(~50\%\) during the hours surrounding noon.
Preliminary Results from Padonia, MD Ground Site

\[ \Delta \text{NO}_2 = \text{NO}_2 \text{ FRM} - \text{NO}_2 \text{ photo} \]

- The interference in the FRM monitor over predicts by ~50% during the hours surrounding noon.
• Currently conducting an intercomparison of direct optical, photolytic conversion, and FRM monitors throughout the summer months.

• Site operational with all monitors starting in mid – February 2012.

• Glass inlet, 5 m AGL, all instruments sample from common sampling manifold.
## Monitors Tested

<table>
<thead>
<tr>
<th>Manufacturer and Model</th>
<th>Operation Principle</th>
<th>FRM/FEM status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teledyne T200U</td>
<td>Moly-chemiluminescence</td>
<td>FRM</td>
</tr>
<tr>
<td>Teledyne 200EUP</td>
<td>Photolytic-chemiluminescence</td>
<td>FEM (application approved, designation imminent)</td>
</tr>
<tr>
<td>Aerodyne CAPS (both versions: fast response and ambient)</td>
<td>Cavity attenuated phase shift</td>
<td>--</td>
</tr>
<tr>
<td>Los Gatos Research CRDS</td>
<td>Cavity ringdown spectroscopy</td>
<td>--</td>
</tr>
</tbody>
</table>
## Instrument Specifics

<table>
<thead>
<tr>
<th>Manufacturer and Model</th>
<th>Size (h x w x l)</th>
<th>weight (lbs.)</th>
<th>Power (W)</th>
<th>Sample flow, vol (Lpm)</th>
<th>Cost ($USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teledyne T200U</td>
<td>7”x 17”x 24”</td>
<td>55</td>
<td>500</td>
<td>1.0</td>
<td>~16K</td>
</tr>
<tr>
<td>Teledyne 200EUP</td>
<td>7”x 17”x 24”</td>
<td>61</td>
<td>600</td>
<td>1.1</td>
<td>~25K</td>
</tr>
<tr>
<td>Aerodyne CAPS (both versions: fast response and ambient)</td>
<td>9”x 17”x 26”</td>
<td>27</td>
<td>&lt;100</td>
<td>0.9 (ambient) 4.5 (fast)</td>
<td>~25K</td>
</tr>
<tr>
<td>Los Gatos Research CRDS</td>
<td>7”x 19”x 24” (plus external drier)</td>
<td>60</td>
<td>100</td>
<td>0.9</td>
<td>~30K</td>
</tr>
</tbody>
</table>
Nightly span/zero cycle

Gas-phase titration of NO (excess) with $O_3$

Bottled NO$_2$ gas

![Graph showing NO and NO$_2$ concentrations over time](image)
March 2012 Span/Zero checks

- Instruments within 15% of low span check and within 10% of high span check.
Initial Performance Characterization

- EPA’s AIRS site – RTP, NC; March 2012

\[ R^2 = 0.999 \]

\[ R^2 = 0.99 \]

\[ R^2 = 0.98 \]

\[ R^2 = 0.99 \]
## Operational Experiences

<table>
<thead>
<tr>
<th>Manufacturer and Model</th>
<th>Data Interface/Accessibility</th>
<th>Calibration Procedures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teledyne T200U</td>
<td>- easily interfaced to our Envidas Ultimate data logger</td>
<td>- zero, high NO span to set slope and offset</td>
</tr>
<tr>
<td>Teledyne 200EUP</td>
<td></td>
<td>- zero, high NO span to set slope and offset; then determine conversion efficiency using NO₂</td>
</tr>
<tr>
<td>Aerodyne CAPS (both versions: fast response and ambient)</td>
<td>- Currently not interfaced with our data logger; operates using Aerodyne software which generates .txt files (comma delimited)</td>
<td>- Multipoint calibration periodically suggested to compare with factory calibration. Manual baseline check required weekly.</td>
</tr>
<tr>
<td>Los Gatos Research CRDS</td>
<td>- Can be interfaced with data logger via the provided 0-5V analog out signal; however no ‘status’ flag provided (yet); using .txt files generated by the instrument (tab delimited)</td>
<td>- Automatically checks the baseline signal at user defined interval; no further calibration required.</td>
</tr>
</tbody>
</table>
ORD's Current Initiatives for NO$_2$ (FY12- FY15) include:

- Method inter-comparison through the summer
  - Including detailed NO$_y$ and reduced nitrogen speciation to look at potential interferences
- Develop calibration procedures for direct measurement techniques
  - NO$_2$ cylinder vs GPT
- Detailed laboratory based assessments
  - Interference testing
  - 40 CFR part 53 subpart B performance testing
- Develop and document performance criteria including calibration and challenge procedures
- Evaluate optical monitors in a near-roadway environment
Acknowledgements

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**Disclaimer:**
Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.